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Ion exchange membranes as separators in microbial fuel cells for bioenergy conversion: A comprehensive review

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A B S T R A C T

The urgent need to address the twin problems of the modern world, energy insecurity caused by fossil fuel depletion and climate change caused by global warming from carbon dioxide emission and the greenhouse effect has led to among other things the emergence of fuel cell technology as a green energy technology that could generate cleaner and highly efficient energy. Microbial fuel cell (MFC), an emerging dual function, bioenergy conversion device, that not only treats wastewater but also generates electricity, has caught much attention of both fuel cell and bioenergy researchers. Until today, the commercialization of MFC has been restricted mainly due to its high cost and low power density. Many challenges still remain to be conquered, in order to improve the performance and commercialization of MFC. It is generally known that ion exchange membrane in MFC is one of the main factors that could significantly affect the cost and performance of MFC. This review provides an overview of several important membrane characteristics, which include membrane internal resistance, membrane biofouling, pH splitting, oxygen diffusion, and substrate loss across the membrane. The negative impact of these characteristics on MFC performance, are discussed. Moreover, this review concerns the types of membrane that have been applied in MFC systems, such as cation exchange membranes, anion exchange membranes, membraneless technology, polymer/composite membranes, and porous membranes. The future trend of membrane development for MFC applications is also discussed.

Contents

Abbreviations: PEMFC, Proton Exchange Membrane Fuel Cells; AFC,, Alkaline Fuel Cells; PAFC, Phosphoric Acid Fuel Cells; MCFC, Molten Carbonate Fuel Cells; SOFC, Solid Oxide Fuel Cells; DMFC, Direct Methanol Fuel Cells; DFAFC, Direct Formic Acid Fuel Cells; MFC, Microbial Fuel Cells; CI, Current Interruption; EIS, Electrochemical Impedance Spectroscopy; HFR,, High Frequency Resistance; DO, Dissolved Oxygen; CEM, Cation Exchange Membrane; AEM, Anion Exchange Membrane; ORR, Oxygen Reduction Reaction; SEM, Scanning Electron Microscopy; PEM, Proton Exchange Membrane; MEA, Membrane Electrode Assembly; COD, Chemical Oxygen Demand; CE, Coulombic Efficiency; SPEEK, Sulfonated Polyether Ether Ketone; BPSH, Disulfonated poly (arylene ether sulfone); DS, Degrees of Sulfonation; PES, Poly(Ether Sulfone); CNF, Carbon Nanofiber; PECVD, Plasma Enhanced Chemical Vapor Deposition

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1. Introduction

Mankind's changing lifestyle, which has become more energy intensive, needs a secure, sustainable supply of energy to power homes, factories and offices, and more recently, to power increasing numbers of personal devices. Most of the energy comes from non-renewable primary energy sources, namely fossil fuels such as coal, natural gas and oil, all which will run out in the near future. Coal, the first fossil fuel to be exploited, is expected to be depleted by the year 2112, while more recently used fossil fuels, oil and natural gas, will be exhausted even earlier (i.e., by year 2040 and 2042, respectively) [1]. In addition, extensive energy production from fossil fuel combustion has caused wide spread pollution of the atmosphere by NO_x and SO_x emissions, resulting in serious global environmental problems, such as global warming, due to carbon dioxide emissions and the greenhouse effect, which has led to climate change on a global scale. The emergence of clean, zero emission fuel cell technology in recent years has provided a sustainable and efficient means of reducing carbon emissions from electrical power generation and transportation. Many types of fuel cells have been developed over the years, including PEMFC, AFC, PAFC, MCFC, SOFC, DMFC, DFAFC, and MFC. AFCs are not only very well known for providing auxiliary power to NASA's Apollo spacecraft, but have also been used to provide auxiliary power in early hybrid vehicles [2]. PEMFCs have been applied mostly to power fuel cell vehicles because of their high power density and efficiency [3] whilst PAFC [4], SOFC [5] and MCFC [6] have been used mainly as stationary, distributed power generation plants in smart grids and in combined heat and power (CHP) applications because of their high operational temperatures. DMFCs are mainly applied to power portable electronic devices because of their high power density compared to lithium ion batteries and the ease of handling of liquid methanol compared to hydrogen [7]. MFC, an emerging fuel cell technology, has drawn great interests from fuel cell as well as bioenergy researchers in recent years because they have the potential to not only generate electricity like other fuel cells, but to simultaneously treat wastewater, a bioenergy resource [8,9].

MFCs are basically bioreactors that use bacteria as electrocatalysts to convert the bioenergy of biomass in wastewater into electrical energy [10]. MFCs commonly consist of an anode and a cathode, either separated by a proton exchange membrane that acts as a solid electrolyte bridge or connected directly via the wastewater substrate that also acts as an electrolyte bridge. At the anode, anaerobic microbes acting as biocatalysts oxidize the organic constituents of the wastewater, which is also called the substrate, to generate protons, electrons, and carbon dioxide gas. Protons migrate to the cathode from the anodic chamber through the membrane or directly across the wastewater in the case of membrane-less MFCs. In addition, electrons migrate to the cathode through the external circuit in order to complete the circuit and generate electrical power. They then combine with the protons to form water if the electron acceptor is oxygen, or ferrocyanide if the electron acceptor is ferricyanide [11].

Various configurations of MFCs have been developed: dual chamber MFCs, single chamber MFCs, tubular MFCs, plate MFCs and stacked MFCs. The anode and the cathode of a dual chamber MFC are placed in two distinct compartments that are separated by a proton exchange membrane. In contrast, the cathode of a single chamber MFC is not located in an aerated chamber but is directly exposed to the air, leaving the MFC with only a single anode chamber. The cathode and anode of this type of MFC are usually hot pressed together with the membrane to form a MEA [12]. Fig. 1 shows the schematic diagrams of the dual chamber and single chamber MFCs [13].

Tubular MFCs, as the name belies, have a cylindrical or tubular shape rather than a rectangular shape, where the MEA is wrapped around a central anode chamber and the cathode is exposed to the air, as shown in Fig. 2 [14]. Plate type MFCs have a flat rectangular shape, where the MEA is sandwiched between two non-conductive rectangular plates whose inner surfaces are engraved with flow channels that allow wastewater to flow on the anode side and air to flow on the cathode side in much the same way as the PEMFC, as shown in Fig. 3 [11]. MFCs can also be scaled up by arranging them in a stack, either in series or in parallel, like other fuel cells, in order to produce higher voltage or larger current densities respectively, as shown in Fig. 4 [15].

Although the MFC has the dual function advantage of simultaneous wastewater treatment and generating electricity over other low temperature fuel cells, such as the PEMFC and DMFC, its high cost [16] and low power density [17] still prohibit commercialization. The membrane separator is one of the main components of the MFC that could significantly affect its overall cost and power density. Hence, the main objectives of this review are to investigate how the membrane′s internal resistance could affect MFC performance and how the membrane could act as a physical barrier to inhibit oxygen diffusion and substrate crossover between the two chambers of the MFC. Furthermore, the review will elucidate how biofouling on the

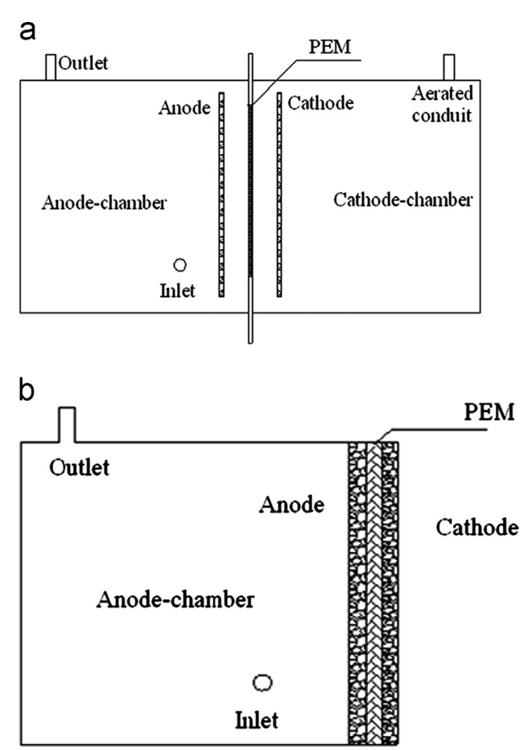


Fig. 1. (a) Dual chamber MFC, (b) Single chamber MFC [13].

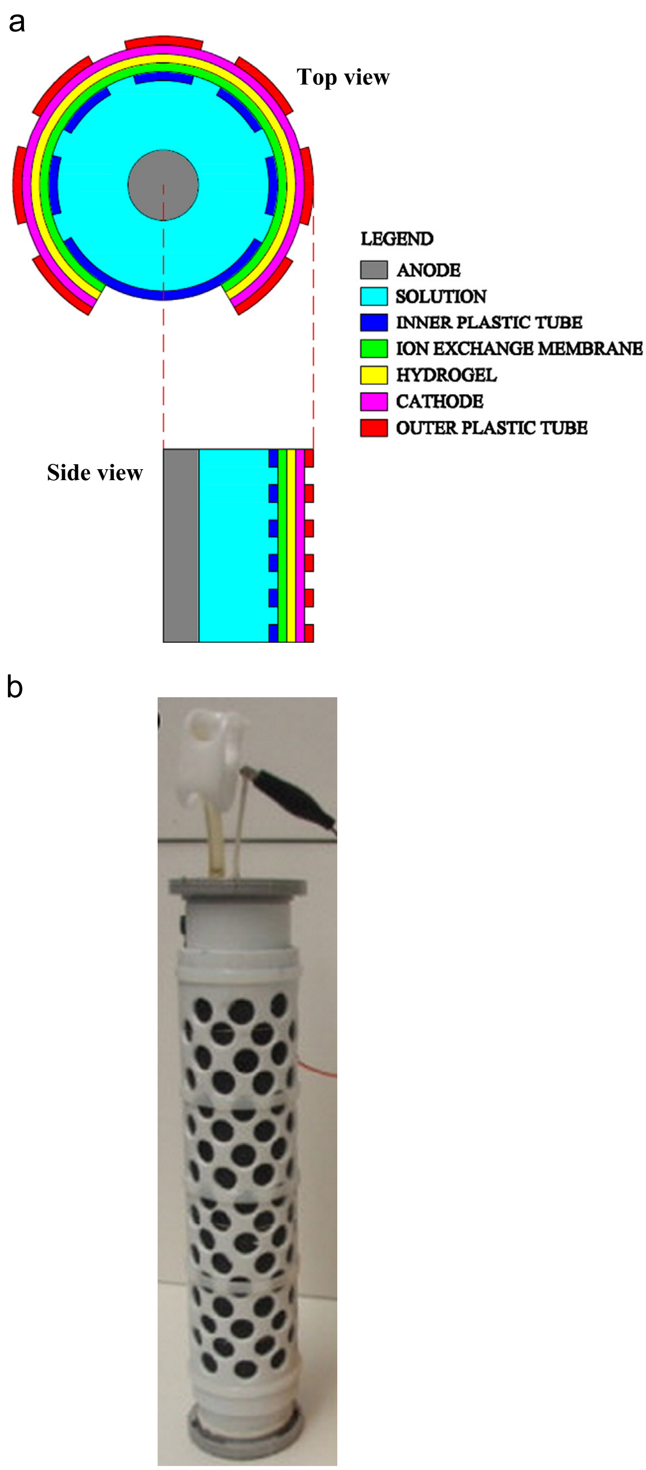


Fig. 2. (a) Modified schematic diagram of tubular MFC (top view and a partial side view), (b) Picture of tubular MFC [14].

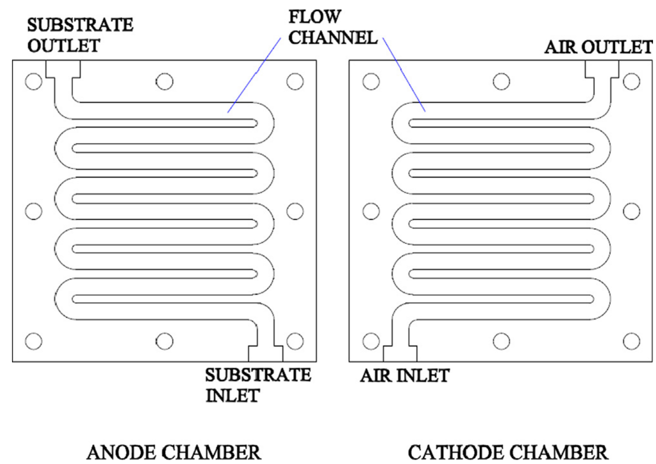


Fig. 3. Modified schematic diagram of plate type MFC (Cathode chamber is mirror to anode chamber) [11].

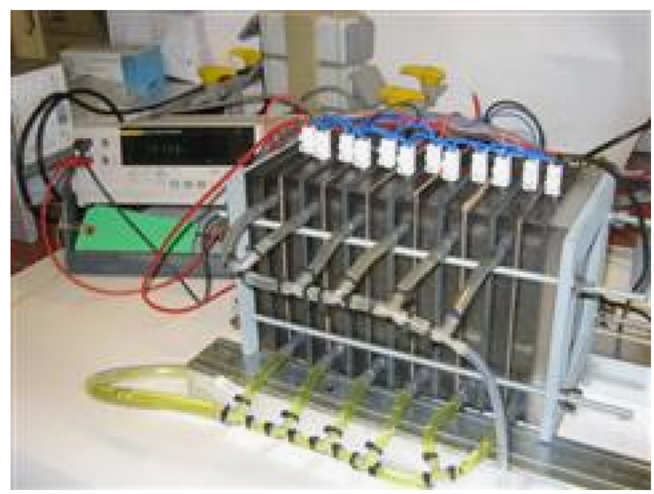


Fig. 4. MFC in parallel stack arrangement [15].

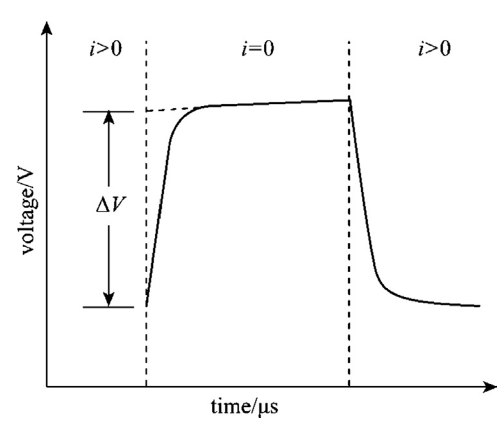


Fig. 5. Voltage waveform during current interruption [30].

membrane's surface and pH splitting across the two chambers occur. Until today, various types of membranes have been used in MFC; but the Nafion® membrane remains the most common membrane used. However, the high cost of Nafion® membrane has led to the development of other cheaper membranes [18,19]. Hence, the review aims to appraise the properties of the major types of membranes commonly used in MFCs: the cation exchange membranes, the anion exchange membranes, the polymer/composite membranes and other miscellaneous types of membrane.

2. Effects of membrane separators on MFC performance

2.1. Membrane resistance

Most of the total resistance of an MFC in operation is contributed by the internal resistance [20], which consists of the resistances of the anode, the cathode, the electrolyte and the membrane [21]. The

performance of MFCs with high resistance membranes is often low because of the low ion exchange capacity of the membrane that reduces proton diffusion from the anode to the cathode, leading to low current and power densities [22]. On the other hand, the performance of MFCs with porous low resistance membranes, such as microfiltration membranes, is also low because oxygen and substrate crossover through the membrane pores reduce CE and power density [23]. Hence, new types of membranes are often non-porous but have low membrane internal resistance to facilitate proton transfer.

Membrane resistance is influenced by the nature of the electrolyte, pH and concentration of the electrolyte solution [24]. Since in general ohmic resistance is the most dominant constituent of membrane resistance in a fuel cell system, it can be used to estimate the membrane resistance in MFCs [25–27]. Although there are many techniques available for measurement of the ohmic resistance in a fuel cells, such as CI, EIS, AC resistance and HFR [28], the most common techniques used are the CI and EIS techniques [29,30]. The CI technique [23] measures the membrane resistance by interrupting the cell current and measuring the difference in voltage before and after the interruption, as shown in Fig. 5 [30]. Ohmic resistance is then obtained using Ohm's law, which is $R_{\Omega}=\Delta V/I$ [30]. However, the interruption period must be short enough (or the frequency of the measurement must be high enough), probably less than 10 μs, in order to precisely measure the small value of the cell's resistance. Moreover, the measurement must be rapid enough to prevent overestimating the voltage changes [23].

Recently, the EIS technique has become preferred over the CI technique because the former can measure internal resistances, such as the charge transfer resistance, the double layer mass transfer resistance and the ohmic resistance, separately for each component of the MFC that contributes to the total internal resistance [26,31]. In addition, low amplitudes (5–10 mV peak-to-peak) used in the EIS technique helps to reduce measurement errors [32]. In this technique, the MFC is subjected to a range of frequencies (typically 10 kHz–1 Hz) and the variations in the cell voltage and current are measured [28,30]. EIS results are normally represented by either Nyquist plots, where the imaginary part of the impedance is plotted against the real part of the impedance or Bode plots, where the magnitude of the impedance is plotted against frequency, as shown in Fig. 6(a) and (b) respectively [23]. The ohmic resistance in Nyquist plots corresponds with the point at the left pass of the curve (the curve cut at real axis) whereas in Bode plots, it corresponds with the resistance at the highest frequency point.

It can be seen that membrane internal resistance should be as low as possible, in order to increase current and power densities. Generally, this can be done by using a conductive membrane that favors the transportation of ions through the membrane [33]. It is not suggested that porous membrane is used as separator in MFC; even though it has low internal resistance compared to non-porous membrane (due to its high oxygen and substrate crossover rate) [34]. When membrane only internal resistance measurement is required, it is recommended that the EIS technique is used, rather than the CI technique; because EIS has more advantages than the CI technique [26,31].

2.2. Oxygen diffusion

Oxygen diffusion from the cathode to the anaerobic anode chamber is a very important issue in MFCs because MFC performance is reduced by voltage loss through a rise in redox potential due to substrate consumption or loss by aerobic rather than anaerobic bacteria [35,36]. Moreover, since oxygen is the more favorable electron acceptor, it competes with the anode to accept electrons, hence reducing the CE of the MFC [35,37]. It was

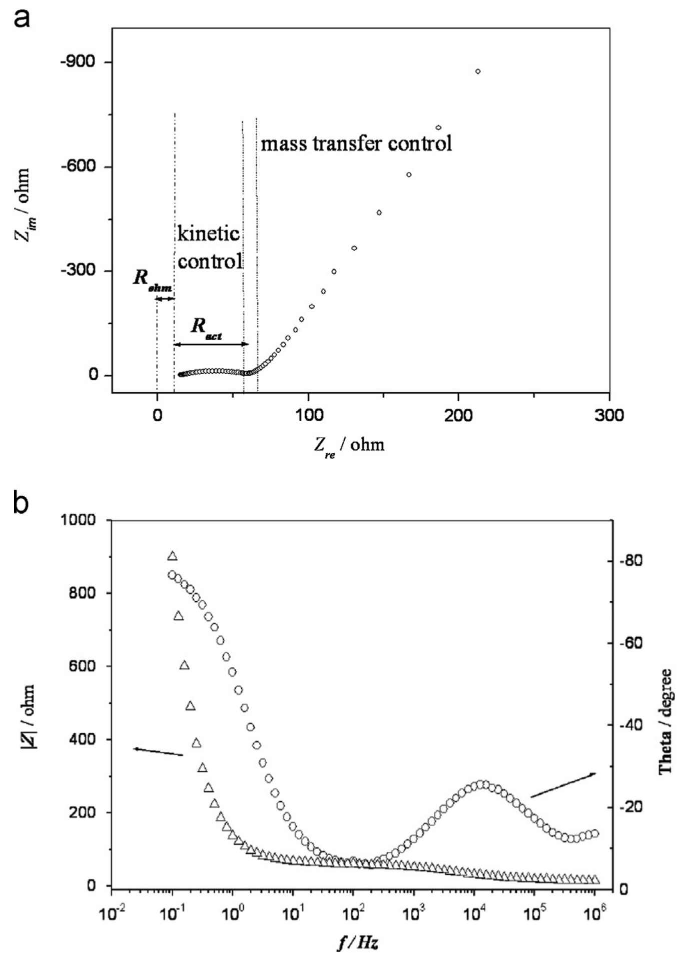


Fig. 6. (a) Nyquist plot, (b) Bode plot [23].

reported that the CE for membraneless MFC was less than 20%, which is lower than MFC with membrane [38]. However, MFC performance is not permanently affected by oxygen diffusion since anaerobic bacteria can continue to function once oxygen is eliminated from the anodic chamber at any time and MFC power is restored [35]. Oxygen diffusion can be measured by using the apparatus shown in Fig. 7 [39]. Before an experiment starts, nitrogen gas is purged through the system to remove oxygen until the DO level at the DO probe is constant. Air is pumped into a second chamber until the DO level has reached a constant value. The mass transfer coefficient of oxygen through the membrane, k_o (cm s^{-1}), can be calculated as follows [40]:

$$k_o = -\frac{V}{At}\ln\left[\frac{c_o - c}{c_o}\right] \quad (1)$$

where, V is the total volume of the liquid in anode chamber (cm^3), A is the cross-sectional area of the membrane (cm^2), c_o is the initial saturated oxygen concentration in chamber 2 (mol cm^{-3}), and c is the measured oxygen concentration in chamber 1 (mol cm^{-3}) at time t (s). The diffusion coefficient D_o (cm^2 s^{-1}) was calculated using $D_o = k_o L$, where L is the membrane thickness (cm).

The most commonly used non-porous membrane in MFC, the Nafion® membrane, has been proven to be permeable to oxygen [40,41]. This can be seen in one of the studies that reported Nafion® membrane showed the highest oxygen mass transfer coefficient ($k_o = 1.3 \times 10^{-4}$ cm/s) compare to other types of membranes [40]. Porous membranes are known to favor oxygen permeation more so than non-porous membranes because the pores allow dissolved oxygen to diffuse through them at a faster

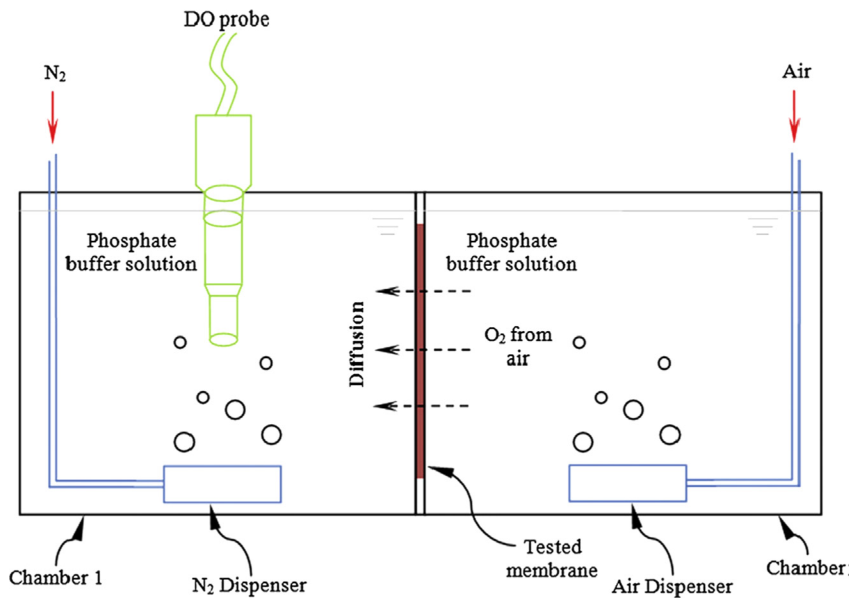


Fig. 7. Apparatus set up for oxygen diffusion determination [39].

rate. In fact, membraneless MFCs have the highest oxygen diffusion rate because there are no physical barriers to prevent oxygen permeation into the anode chamber [38]. Currently, there are no known membranes that can prevent oxygen diffusion completely; the only way to eliminate the negative impact of oxygen diffusion is by using a chemical oxygen scavenger, such as cystein, in the anodic chamber, which reacts with oxygen to form disulfide dimer (cystine) [36].

Although oxygen diffusions do not bring permanent impact to MFC performance, it still reduces the voltage output and CE of the MFC system [35]. Thus, oxygen diffusion should be minimized (or eliminated) by ensuring that the membrane used is dense (i.e., non-porous) or a chemical oxygen scavenger is used, as mentioned previously.

2.3. Substrate crossover

Like oxygen, substrates in wastewater may crossover by diffusing through membranes from the anaerobic anode chamber to the aerobic cathode chamber when the MFC is in operation, which is the opposite direction of oxygen diffusion. Porous membranes with larger pore size favor substrate crossover more than AEM because the substrates diffuse along the pores at a faster rate [42,43] than in non-porous AEMs, where negatively charged substrates, e.g. acetates, butyrates and propionates, are assisted by the anion transfer property of AEMs to diffuse across solid membranes at a slower rate [44]. Substrate crossover is usually tested in a dual chamber MFC, where the anode chamber contains a known concentration of substrates and the cathode chamber is filled with distilled water. Substrate concentrations in both chambers are then measured during MFC operation using gas chromatography equipped with a flame ionization detector and a capillary column [22].

When substrates diffuse into the cathode chamber, they are oxidized on the cathode surface by aerobic bacteria, producing extra electrons for the ORR at the cathode, which creates an internal short circuit inside the MFC that reduces CE [34,42,45]. The formation of a biofilm by aerobic bacteria on the cathode because of substrate crossover is generally known as biofouling of the cathode surface [42,46,47]. Biofilm has been reported to have increased the power density of MFCs during the early phase of MFC operation because the presence of electrons generated by aerobic bacteria promotes ORR on the cathode, as shown in Fig. 8

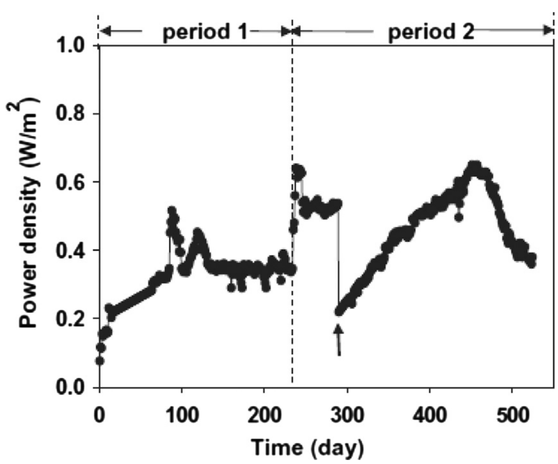


Fig. 8. Power density increased in the early stage and starts to decrease when cathodic biofilm is removed on day 290 (indicates by arrow) and decreased after day 467 due to thick cathodic biofilm [48].

[48]. However, the power density then drops significantly after the MFC is operated over a long period of time because the thickening biofilm gradually reduces both oxygen diffusion to the cathode and the cathode active surface area available for the ORR [48]. Hence, it is concluded that substrate crossover should be avoided in order to ensure continuous power generation over long-term operation of an MFC. As long as the membrane is non-porous and allows cations (but not anions) to cross, substrate crossover issues can be overcome.

2.4. Biofouling

Membrane biofouling normally occurs on the membrane surface facing towards the anode chamber of the MFC by attachment of bacteria and organic substrates to form a biofilm that is less homogenous than the biofilm on the anode surface [41]. Oxygen diffusion from the cathode chamber through the membrane encourages aerobic bacteria to form additional biofilm on the same membrane surface [41]. The aerobic bacteria in the membrane biofilm consume the crossover oxygen, creating a negative oxygen gradient towards the anode side that causes more oxygen

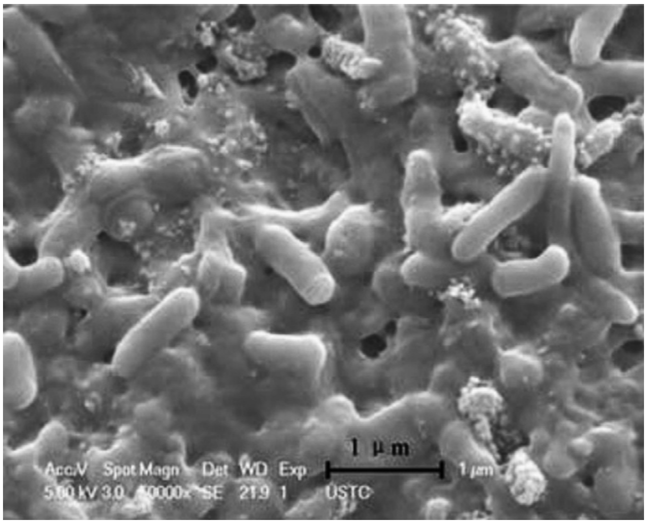


Fig. 9. SEM image of membrane surface that was fouled [50].

to diffuse from the cathode chamber into the anode chamber [41]. Moreover, the biofilm also acts as a physical barrier for proton transfer from the anode chamber to the cathode chamber, which increases both the pH gradient between them and the electrical resistance of the MFC [49], the former deteriorating bacterial growth, which reduces MFC performance further [50]. To maintain top MFC performance, the fouled membranes have to be replaced with new membranes, which increases MFC operational cost [50].

Although there is no specific method to directly measure the biofouling rate, examination of the surface morphology of the fouled membrane using SEM can indicate the physical extent of biofouling, as shown in Fig. 9 [49–51]. Measuring the change in ion exchange capacity, specific proton conductivity and electrical resistance of the fouled membrane can indicate the extent of deterioration of membrane function as an effective separator [50,52]. In addition, the effect of fouled membrane on MFC performance can be assessed by measuring the open circuit voltage and power density of MFCs during operation [50]. Fouled membranes have been found to exhibit the highest internal resistance, produce the lowest power density (20.9 mW/m^2 for fouled membranes, 52.8 mW/m^2 for un-fouled membranes and 100 mW/m^2 for pre-treated membranes) and the lowest COD removal (28% for fouled membranes, 46% for un-fouled membranes, and 87% for pre-treated membranes) and CE (3.3% for fouled membranes, 5.9% for un-fouled membranes, and 13.7% for pre-treated membranes) as compared to un-fouled and pre-treated membranes [53]. Internal resistance of MFCs using a Nafion® membrane as the separator has been found to increase because of attachment of anolyte cations on sulfonate functional groups that prevent proton transfer, rather than membrane biofouling [52]. However, this effect is observed only when the biofilm is thinner; its effect is negligible in large scale MFCs that operate over a long term, where the effect of the thicker biofilm is more severe.

Membrane biofouling can be reduced or eliminated by using either the anti-microbial approach, in which the membrane or its surface is chemically modified to kill bacteria that adhere to the membrane surface, or the anti-adhesion approach, in which the chemically modified membrane or its surface prevents substrate adsorption and cellular adhesion while retaining membrane function [54]. The anti-microbial approach includes biocides such as silver [55], copper and TiO_2 particles [56], in composite membranes or to coat the surface of existing membranes with the heavy metal biocides such as nano silver particles [57] or long chain polymers that disrupt bacterial cell walls, such as quaternized 2-(dimethylamino) ethyl methacrylate (qDMAEM) grafted on commercial polyvinilidene fluoride (PVDF) [58]. However, there is a high risk of biocides leaching into the anode chamber and causing cell death that may eventually stop MFC operation. The anti-adhesion approach modifies the hydrophilicity of the membrane or the membrane surface by incorporating polyethylene glycol (PEG) [59], or the electrical property with polycation or polyanion so that the membrane surface become either negatively charged to prevent adhesion of negatively charged bacteria [60] or positively charged to prevent adhesion of positively charged bacteria [61]. However, membrane hydrophilicity can only prevents initial biofouling [56]; once a membrane starts to foul it cannot stop the biofouling [49]. A novel anti-adhesion method is to grow a well-ordered, dense-array sharp-tip nanostructures that prevent bacterial adhesion, but the approach remains undeveloped [62]. Since the anti-adhesion approach often does not prevent biofouling completely, a combined approach of anti-adhesion and anti-microbial techniques could prevent biofouling over a longer period of membrane operation [58].

Based on the above discussion, it is known that the biggest challenge of membrane technology in MFC applications is biofouling. Biofouling will deteriorate membrane performance and reduce its durability. Subsequently, the power output of MFC will be affected and the operational cost of MFC will increase [50]. Until now, despite no real solutions to totally prevent biofouling formation on membrane surfaces, researchers have tried to reduce biofouling formation through anti-adhesion [59–61] and anti-microbial techniques [55,56], as mentioned earlier. In the future, a novel anti-biofouling technique should be developed that is able to prevent biofouling formation on membrane surfaces, which does not disturb the anaerobic bacteria activities in anode solution as well.

2.5. pH splitting

Membrane separators, used to help reduce oxygen diffusion and substrate crossover in MFCs, gradually causes a wide variation of pHs between the anode and cathode chambers during the MFC operation called pH splitting, which can drastically reduce MFC performance. After the MFC operates for some time, the anolyte gradually becomes more acidic while the catholyte gradually becomes more alkaline rather than neutral. The level of pH splitting depends on the types of membrane separator. MFCs using CEM as separators encounter severe pH splitting problems compared to others using AEM [44,63,64] because the higher concentration of cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH^{4+}) in the anolyte compared to protons, which compete with protons for attachment to negatively charged functional groups in the CEM (e.g. sulfonate group in Nafion® membrane) [41]. Reduction of protons shuttling to the cathode chamber causes protons produced during biocatalytic activity by anaerobes to accumulate in the anodic chamber, which decreases the pH of the anolyte. Acidic conditions in anolytes suppress oxidation activity of bacteria, which reduces proton production further [65–68]. Fewer protons migrating to the cathodic chamber is not sufficient to replenish protons consumed by oxygen reduction reaction (ORR) at the cathode, which limits the ORR rate at the cathode [69] and increases the pH of the catolyte [40]. On the other hand, since the anions are responsible for proton transfer in AEM, there are no cations available to compete with protons for attachment on the AEM surface. Hence, proton transfer rate is not limited, which produces a lower rate of pH splitting.

The optimum anolyte pH for single chamber air cathode MFCs differs from that of dual chamber MFCs. In the former, the highest current density and CE is produced at an anolyte pH of 9 [70] while in the latter, optimum condition is at nearly neutral condition (pH 6.3–7) [66–68]. Although optimum anaerobic bacteria activity occurs at neutral conditions when the anode polarization

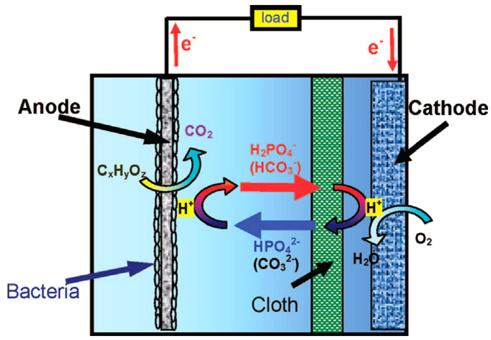


Fig. 10. Mechanism of protons transfer in a single chamber air cathode MFC using phosphate or bicarbonate buffer solutions [72].

resistance is the lowest, the reaction in the air cathode, which is the rate limiting step and favors alkaline condition because its polarization resistance decreases with anode alkalinity, changes the optimum pH condition at the anode from 7 to a more alkaline pH (pH 9 in this case) [70]. Anaerobic oxidation reactions are not favoured in acidic anolytes for either types of MFCs since open circuit voltage, current and power generation of MFCs are found to be much lower in acidic anode conditions compared to those at neutral conditions [71].

One popular method for pH splitting in MFCs is by using buffer solutions, such as phosphate and bicarbonate buffers [72], which can not only maintain pH conditions for optimum anaerobic bacteria activity but also can increase solution conductivity and hence could compensate for slow proton transfer [73]. Proton transfer mechanisms for both buffer solutions are shown in Fig. 10 [72]. A single chamber air cathode MFC using a pH 9 bicarbonate buffer (0.2 M) is found to generate a power density of 1550 W/m^3 (2770 mW/m^2), which is 39% higher than that generated by a similar MFC using a pH 7 phosphate buffers. The superior performance of single chamber MFCs using pH 9 bicarbonate buffer solution is not because of anaerobic activity, which may not be the limiting factor for pHs less than 9 [70]. The slower loss of bicarbonates by conversion into CO_2 to compensate for lower CO_2 vapor pressure at pH 9 retains higher bicarbonate concentration and solution conductivity which improves proton transfer [72]. Apart from buffer solutions, common pH control agents such as sodium and ammonium hydroxide have been used to maintain anolyte pH in MFCs. However, to prevent anolytes from becoming acidic, ammonium hydroxide is preferred because the ammonium ion vaporizes into ammonia gas after helping to shuttle protons to the cathode [65]. In short, in order to optimize the anaerobic bacteria catalytic activities, the optimum pH of anode solution (i.e., neutral for dual chamber MFC and slightly alkaline for air cathode MFC) must be preserved by using proper buffer solutions [70,72].

3. Common membrane separators used in MFCs

3.1. Cation exchange membrane

CEM such as Nafion® [74–77], Hyflon® [78], Zirfon® [79] and Ultrex® CMI 7000 [80–83] have long been the preferred separators for MFCs because they easily conduct protons generated in the anode chamber directly into the cathode chamber. The most commonly used CEM in MFCs, Nafion®, has good proton conductivity because the negatively charged hydrophilic sulfonate group attached to the hydrophobic fluorocarbon backbone promotes proton transport through it [84]. MFCs using thinner Nafion 112 membranes have better performance with higher maximum voltage (670 mV), current (150.6 mA/m^2) and power densities (31.32 mW/m^2) than MFCs using the thicker Nafion 117 membranes (668 mV, 60.28 mA/m^2 and 9.95 mW/m^2) [85] because of the lower ohmic resistance of the former [86]. However, thinner membranes favor oxygen and substrate permeability, which can drastically lower the CE of MFCs [77]. When compared to other types of separators such as salt bridges [77], Ultrex® CMI-7000 (CEM), and Fumasep FAD (AEM) [24], Nafion® 117 membranes often have lower internal resistance and produce higher power densities. However, the performance of Nafion® 117 and Ultrex® CMI-7000 membranes are comparable since they generate almost similar power densities [87].

MFCs with oxygen diffusion cathodes using thinner Hyflon®, a CEM containing perfluorosulfonylfluoridevinyl ether membranes, exhibit higher mean voltage, mean current density and mean power density than similar MFCs with thicker Hyflon® membranes [78] because of the lower membrane resistance of thinner membranes in the same way as Nafion. Further study of four-cells MFC stacks shows that the MFC stack using Hyflon® produced lower quality performances than a similar MFC stack using a standard PEM [78]. However, this result is inconsistent because the lower performance is caused by voltage reversal in one of the cells, a phenomenon caused by fuel starvation, causing bacterial activity to drop, which could also occur in the MFC stack using the standard PEM [88]. Zirfon®, an ultrafiltration composite membrane made of an asymmetric polysulfone membrane structure containing inorganic filler particles of ZrO_2 which is also a CEM [89], has a higher oxygen mass transfer coefficient (1.9×10^{-3} cm/s) than Nafion® 117 (2.8×10^{-4} cm/s), and a lower specific ionic resistance (2727 Ω cm) than Nafion® 117 (17,000 Ω cm) and Fumasep® (16,000 Ω cm), another CEM, because its larger mean pore size favors ion transfer and oxygen diffusion [79]. Tubular MFCs with air cathodes using Ultrex® CMI-7000, a CEM membrane in membrane electrode assemblies, have higher voltages and power densities when the membranes are filled with hydrogel [14]. The MFCs also produced higher power density (6.1 W/m^3), greater CE (71%) and lower electrolyte and polarization resistance (0.23 Ω) than MFCs when using a AEM membrane Ultrex® AMI-7001 (power density 4.9 W/m^3, CE 63% and resistance 0.69 Ω) [14].

The main problems of using Nafion® and other CEMs as separators in MFCs are pH splitting between the anode and cathode chambers caused by proton accumulation in the anode chamber [90], oxygen diffusion from the cathode to the anode chamber, substrate loss and biofouling [41].

Nafion® 117 membrane is still undeniably the most commonly used membrane in MFC applications, because of its good conductivity [84]. It is recommended that Nafion® 117 membrane should be modified to improve its properties, such as preventing biofouling formation on its surface easily, and reducing oxygen and substrate crossover.

3.2. Anion exchange membrane

Attempts to solve CEM problems, especially pH splitting, have led to the development of AEM that conduct hydroxide or carbonate anions from the cathode to the anode chamber, facilitating proton transfer by acting as proton carriers [91]. This proton transfer mechanism, which is dominant in RALEX™ AEM for example, avoids proton accumulation in the anode chamber and reduces pH splitting (ΔpH 0.27), which improves MFC performance over Nafion® 117 (ΔpH 1.8) [44]. Both AEMs and CEMs in single-chamber MFCs deform in different directions after several operation cycles, as shown in Fig. 11, and the high pH solution accumulating in the voids reduces MFC performance, especially for AEMs because of larger voids [63]. However, AEM performance recovers after re-pressing the AEM-MEA and is higher compared to similarly treated CEM [63]. Among the three different common types of AEMs, AFN, AM-1 and ACS, AFN membrane resistance is the lowest, which consequently produces the highest current

density (0.38 mA/cm^2), followed by AM-1 (0.28 mA/cm^2) and ACS (0.21 mA/cm^2) membrane [22]. On the other hand, AM-1 and ACS have lower oxygen transfer coefficients (0.98×10^{-4} cm/s and 0.65×10^{-4} cm/s, respectively) and maximum oxygen flux (2.3×10^{-8} mmol/s cm^2 and 1.6×10^{-8} mmol/s cm^2, respectively) than AFNs (oxygen transfer coefficients 1.26×10^{-4} cm/s and maximum oxygen flux 3.0×10^{-8} mmol/s cm^2) [22]. Table 1 lists the performance of AEM membranes used in MFCs.

It can be concluded that one of the good properties of AEM, compared to CEM, is the elimination pH splitting issues [44]. Besides, MFC showed better performance with AEM, as its ion exchange separator, compared to CEM (as shown in Table 1). However, a major drawback of AEM is that it favors substrate crossover [44]. This can promote biofouling formation on cathode surfaces, which then reduces MFC performance [42,48].

3.3. Membraneless MFCs

The major problems associated with membrane separators in MFCs, such as biofouling, limited proton transfer rate and high membrane costs, could be avoided by removing the membrane separators altogether into membraneless MFCs [92,93], which are proven to have lower cell internal resistance [94]. The high proton transfer rate in membraneless MFCs is also associated with high oxygen diffusion towards the anode, which causes the CE of the MFC to drop drastically by about 20% more than MFCs with membranes [14,38,63], even with higher power densities [46]. Moreover, membraneless MFCs suffer from the tendency to form biofilms on cathode surfaces because the substrates easily reach the cathodes without hindrance [46,47]. The biofilm limits oxygen diffusion to the cathode and hence reduces MFC performance [95]. An innovative membraneless MFC design avoids oxygen diffusion from the cathode chamber to the anode chamber by forcing electrolytes to flow continuously from the anode chamber to the cathode chamber, which promotes proton flow but limits oxygen diffusion in the opposite direction [96]. The COD removal efficiency in this type of membraneless MFC could reach as high as 90.5%, but most of it occurs mostly in the cathode chamber by aerobic bacteria [96].

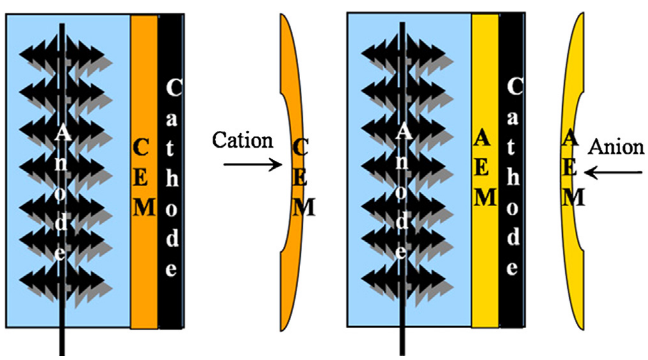


Fig. 11. Deformation of CEM and AEM in single chamber MFC [63].

There are undeniably many advantages of membraneless technology i.e., no membrane biofouling issues, zero membrane internal resistance, and lower MFC operational costs [92,93]. However, membraneless technology is not ideal for long term MFC operations, because of its high oxygen and substrate crossover rate, which can severely deteriorate the performance of the MFC [14,38,46,63,97].

3.4. Polymer/composite membrane

Sulfonated polymer membranes containing sulfonate groups such as SPEEK membranes [98–102] and BPSH membranes [103] are now increasingly being used to replace the more widely used Nafion® membrane in MFCs to overcome the shortage of Nafion® membranes and to lower MFC cost [41]. SPEEK membranes are produced by sulfonating the cheaper, chemically and thermally stable and mechanically strong native PEEK membranes in order to increase proton

Table 1
Types of AEM in MFC.

Types of membrane	Performance	Reference
Ultrex® AMI-7001 (AEM), Nafion® 117, Ultrex® CMI-7000 (CEM), Ultrafiltration membranes (UF-0.5 K, UF-1 K, UF-3 K)	• AEM has the best performance with the highest maximum power density (610 mW/m^2) and CE (72%) compared to other membranes. • All the membranes have almost the same internal resistance ($1230 \pm 44\ \Omega$ till $1308 \pm 18\ \Omega$) except UF-0.5 K ($6009 \pm 58\ \Omega$). • Nafion has the highest oxygen mass transfer coefficients ($k_o = 1.3 \times 10^{-4}$ cm/s). • Substrate mass transfer coefficient UF-3 K (27×10^{-8} cm/s) > UF-1 K (16×10^{-8} cm/s) > AEM (5.5×10^{-8} cm/s) > Nafion (4.3×10^{-8} cm/s) > CEM (1.4×10^{-8} cm/s) > UF-0.5 K (0.89×10^{-8} cm/s).	[40]
Ultrex® AMI 7001, Nafion® 117, Ultrex® CM1 7000, Hyflon®, Zirfon®, Nylon meshes (NY 11, NY 20, NY 41, NY 6 H), Glass fiber filter (GFAPFF, GFAP40) J-cloth, Celgard®, SciMat®	• Ultrex® AMI 7001, Celgard®, Nylon meshes (NY 20, NY 41, NY 6 H), GFAP40 and J-cloth have the lowest pH splitting extent. • GFAPFF and Ultrex® CMI 7000 have highest pH splitting extent. • Porous structured GFAP40 has the highest ionic conductivity. • Nylon meshes (NY11, NY20 and NY41) and Hyflon® have the lowest ionic conductivity. • Ultrex® (both AEM and CEM) membrane have negligible oxygen diffusion coefficient while Celgad® has the highest (10.20×10^{-10} m^2/s). • Ultrex® AMI 7001, Hyflon®, NY11, NY20, NY41, GFAP40, Scimat show high proton conductivity. • Ultrex® AMI 7001 (AEM) is the most suitable candidate as MFC membrane separator.	[64]
Fumasep® FAB (AEM), Nafion® 117(CEM), Fumasep® FBM (BPM), Charge mosaic membrane (CMM)	• AEM has the highest current density among all the membranes. • The BPM with the highest protons/hydroxyl ions transport numbers has the lowest pH increase in cathode, followed by AEM, CMM and CEM.	[120]
Ultrex® AMI-7001 (AEM) and Ultrex® CMI-7000 (CEM)	AEM has higher performance compared to CEM in terms of open circuit voltage and maximum power density at variations of air cathode pressure.	[121]

conductivity [98–102]. Although a Nafion® 117 membrane has a slightly higher open circuit potential than a SPEEK membrane, the latter generates higher power density (670 ± 14 mW/m^2) and CE (75 ± 7%), and has a lower oxygen mass transfer coefficient (1.6×10^{-5} cm/s) [104]. BPSH membranes with higher DS have higher proton conductivity and become more hydrophilic, which reduces the extent of biofouling. On the other hand, the high DS of BPSH membrane causes membrane swelling that allows electrolyte cross-over and accumulation of other cations instead of protons, hence produces a lower power density [103]. The open structure of polycarbonate and nylon nanoporous membranes not only facilitates proton transfer and hence produce higher maximum power density (16 W/m^3) than Nafion® 117 (11 W/m^3), but also allow oxygen to crossover, which reduces anaerobic bacteria catalytic activity [105]. Studies have also shown that Nafion 112/polyaniline composite membrane can produce approximately nine times higher maximum power density (124.03 mW/m^2), compared to Nafion 112 membrane (13.98 mW/m^2), and is comparable to Nafion 117 membrane (133.3 mW/m^2) [33].

Nano-composite polymer membranes, blends of polymer membranes and other polymers or organic/inorganic fillers, take advantage of the properties of individual membranes, such as high conductivity and low cost complimenting each other to compensate for weaker properties of some membranes, such as low strength with stronger properties of others to produce multi-functional composite membranes for MFCs. For example, the cheap, low conducting polymer membrane, PES, when blended with cheap high conducting SPEEK to form a PES/SPEEK 5% composite membrane, produces better MFC performance in terms of the highest maximum power density (170 mW/m^2) and CE (68 ± 6%) than Nafion® membranes because of the presence of sulfonate groups [39]. In the same way, a 15% Fe_3O_4 nano-particle/PES membrane, an inorganic filler/polymer composite membranes, has better MFC performance than Nafion® 117 membranes in terms of maximum power density (20 mW/m^2 for 15% Fe_3O_4 nano-particle/PES membrane and 15.4 mW/m^2 for Nafion® 117 membrane) and open circuit voltage (656 mV for 15% Fe_3O_4 nano-particle/PES membrane and 610 mV for Nafion® 117 membrane) [106]. In addition, an activated CNF/Nafion® (ACNF/Nafion®) membrane, an organic filler/polymer membrane, shows the best MFC performance (maximum power density 57.64 mW/m^2) compared to non-activated CNF/Nafion® composite, Nafion® 112 and Nafion® 117 membranes because the ACNF/Nafion® membrane has smaller pore size, higher porosity and lower surface roughness [107]. However, adding polymer or nano-particles into polymeric membranes can alter the original membrane structure, especially its surface roughness, which increases with greater nano-particle composition. Fig. 12 shows clearly the higher surface roughness of

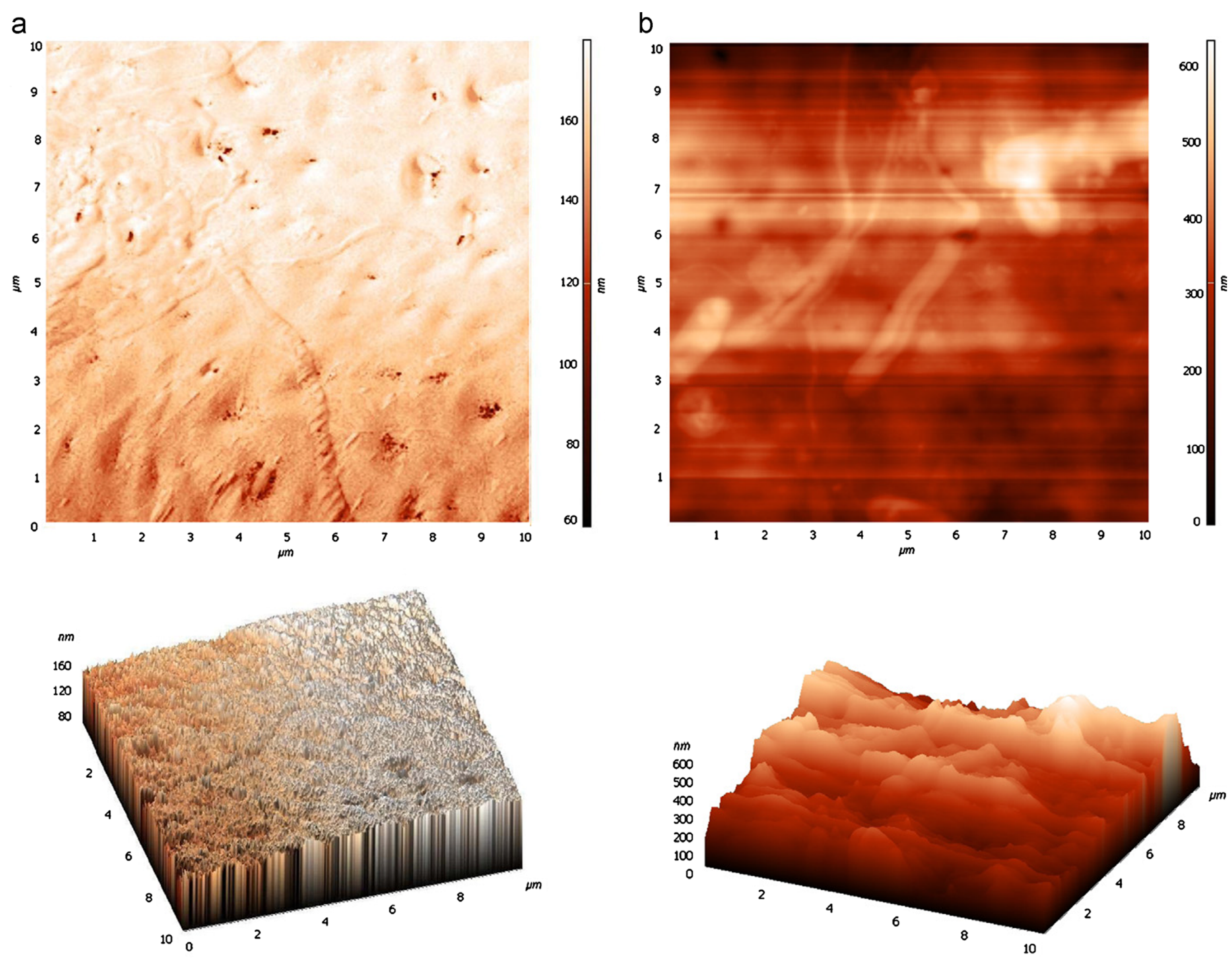


Fig. 12. AFM images from outer surface of two types of Fe_3O_4/PES composite membranes: (a) two and three dimensional images of PES–5% Fe_3O_4 (membrane 1) membrane and (b) two and three dimensional images of PES–20% Fe_3O_4 membrane (membrane 4) [106].

PES–20% Fe_3O_4 membranes compared to PES–5% Fe_3O_4 membranes [106], due to the higher composition of nano-particles of the former. Higher surface roughness favors membrane biofouling, which deteriorates MFC performance [39,106].

Recently, a great deal of research has focused on the synthesis of composite and nano-composite membranes, because they are cheaper and can generate higher power than existing Nafion® membrane [39,104–107]. It is envisaged that nano-composite membranes will play a more critical role in MFCs in the future, because of the promise that nanotechnology could greatly improve their properties.

3.5. Porous Membranes

Porous membranes, such as glass wools [108] and microfiltration membranes [109], have been used as low cost separators in MFCs. Single chamber MFCs using cheap glass wool as separators instead of expensive PEMs are more cost effective for wastewater treatment and power generation [108]. MFCs using microfiltration membranes as separators have been used to decolorize azo dyes, where the porous structure of microfiltration membranes allow oxygen diffusion into anode chambers, degrading the intermediates formed by cleavage of azo bonds [109]. Table 2 lists other types of porous membranes used in MFC application.

Generally, porous membranes also face the same problems as membraneless technology. Its porous structure favors the crossover of bigger molecules, such as substrate and oxygen. The crossover rate is lower than membraneless, but higher than dense membrane [110]. The only good property of porous membrane, is having a low membrane internal resistance [110], which cannot last longer due to biofouling quickly forming on its surface, which subsequently increases its resistance. Hence, porous membrane is not a good candidate as ion exchange membrane in a MFC system.

Table 2
Application of other types of porous membrane in MFC.

Types of membrane	Performance/result	Reference
Selemion HSF, Nafion® 117, polytetrafluoroethylene (PTFE) membrane, Isopore membrane filterand Biomax ultrafiltration disc	• Selemion membrane with lowest internal resistance (1082 ± 193 Ω) and oxygen diffusivities (0.08 cm^2/s) produced the highest power in MFC. • Selemion price ($400/$m^2$) is cheaper than the Nafion® membrane ($1500 m^{-2}).	[122]
Earthen cylinder and Nafion® 117 membrane	• The material structure of an earthen cylinder has lower internal resistance (69 Ω) than the Nafion® membrane (96 Ω), hence increases the rate of proton transfer. • The earthen cylinder produced higher open circuit potential (715 mV), power generation (48.30 mW/m^2), COD removal efficiency (81.8 ± 1.8%) and CE (19.8%) than the Nafion® 117 membrane (open circuit potential 655 mV, power density 28.27 mW/m^2, COD removal efficiency 79.4 ± 2.2% and CE 14.2%).	[123]
Earthen pot and Nafion® 117 membrane	• Earthen pot with lower internal resistance facilitated the proton transfer. • Earthen pot as a MFC separator produced higher open circuit voltage (0.772 V), maximum power density (50 mW/m^2), COD removal efficiency (96.5%) and CE (21.2%).	[124]
Ultrafiltration membrane (UF) and Nafion® membrane	• Maximum power density by UF membrane (53.5 mW/m^2) is just slightly lower compare to Nafion® membrane (55.7 mW/m^2). • pH difference problem did not occur using a UF membrane. • High removal rate of total suspended solid and high COD removal, but low CE due to oxygen diffusion. • Current decrease in long term operation due to substrate crossover and biofilm formation on cathode electrode.	[42]
Cellulose acetate microfiltration membrane (CAMF) and Nafion® 117 membrane	• CAMF membrane has almost similar internal resistance (263 Ω) as Nafion® membrane (267 Ω). • Maximum power density for CAMF membrane (0.831 ± 0.016 W/m^2) was just slightly lower compare to Nafion® membrane (0.872 ± 0.021 W/m^2). • Higher oxygen flux from the cathode to the anode chamber by using CAMF membrane yielded lower CE (38.5 ± 3.5%) than the Nafion® membrane (74.7 ± 4.6%).	[43]
Microfiltration membrane (MF), PEM and membraneless	• Lower internal resistance of MF membrane (248 Ω) compared to PEM (672 Ω) produce highest voltage output (average 0.59 V) and power density (214 mW/m^2) among the tested membranes. • Surprisingly, MF membrane had higher COD removal (96 ± 2.4%) and CE (5.37 ± 0.1%) than the Nafion® membrane (COD removal 92 ± 1.0% and CE 2.53 ± 0.1%). The reported reason was that the high internal resistance of the Nafion® membrane has more of a negative impact towards CE compared to the substrate loss effect in MF membranes.	[110]
Ultrafiltration membrane (UFM-1 K, UFM-5 K, UFM-10 K), microfiltration membrane (MFM) and Nafion® 117 membrane	• Nafion® has the lowest substrate and oxygen diffusion coefficient (D_s=1.47 × 10^{-11} cm^2/s and D_o=3.89 × 10^{-6} cm^2/s) and MFM has the highest (D_s=1.02 × 10^{-6} cm^2/s and D_o=9.96 × 10^{-6} cm^2/s). • UFM-10K with the highest internal resistance (713 Ω) produced the lowest power output (54 mW/m^2). • MFM with the largest pore size produced the lowest CE (7.25%). • UFM-1K with appropriate D_s (2.47 × 10^{-10} cm^2/s), D_o (8.44 × 10^{-6} cm^2/s) and internal resistance (101 Ω) produced the highest maximum power density (324 mW/m^2) and comparable CE (14.5%). Hence, UFM-1K is the most suitable separator used in single chamber MFC for decolorization of Congo red.	[34]

4. Future trends in membrane separator development for MFC application

The review of the problems posed by current membrane separators affecting MFC performance and the type of membranes currently available for MFC application has led to a recommendation of the following as the most important properties membrane separators must possess in order to perform very well in MFCs:

a. Low membrane resistance allows the membrane to facilitate proton transfer from anodic chamber to cathodic chamber.
b. Non-porous or dense membranes prevent oxygen diffusion from the aerated cathode chamber to the anaerobic anodic chamber, substrate crossover in the opposite direction.
c. High biofouling resistance allows MFCs to operate longer without serious drops in performance.
d. Cheaper membrane material reduces MFC's cost.

The Nafion® membrane is currently the most common membrane separator used in MFCs because it is chemically and thermally stable, and has high proton conductivity [111], despite suffering from cation accumulation, oxygen diffusion and substrate loss [41]. Its major drawback is high cost because it alone contributes about 38% of the total capital cost of the MFC [107]. A trade-off between internal resistances, substrate crossover and oxygen diffusion is very hard to achieve. Porous or thinner membranes have low internal resistance, but favor oxygen diffusion and substrate crossover [42,77,86]. Highly porous microfiltration membranes, on the other hand, generate higher power density but lower CE than standard dense Nafion® membranes [34,42]. Although membraneless MFCs have the lowest internal resistance [94], its oxygen diffusion and substrate loss are high and it is prone to biofilm formation on the cathode surface [46,47]. Oxygen and substrate crossover are lower if conductive dense membranes such as cation or anion exchange dense membranes are used, but their internal resistance is higher than porous membrane or membraneless MFCs [42,46]. Until now, none of the membrane separators have been able to avoid the formation of biofilm on its surface. Physical cleaning of the fouled membrane may not totally remove all the foulant [51] whilst chemical cleaning may affect the structure of the membranes [112]. Hence, the membranes have to be replenished once it is fouled severely, which indirectly increases the MFC's cost.

Recently, self-synthesized composite or nano-composite membranes have been developed to improve selected membrane properties, such as membrane hydrophilicity [39,106,107]. Proton conductive materials, such as polybenzimidazoles, polyamides, polyether imides, polysulphones, polyphenylene sulfides, polyetheretherketones and polyphenyquinoxalines, that have long been used to replace Nafion® membranes in PEMFC and DMFC [113], can be used in MFCs by protecting them from being easily fouled by adding hydrophilic nano-particles to make them more hydrophilic and therefore more resistant to biofouling [56]. Such nano-composite membranes can be easily fabricated by the solution casting method [99,114], the sol–gel method [115,116], or the PECVD method [117]. Uniform dispersion of the nano-particles in the nano-composite membranes is important to ensure more uniform membrane properties, which could be obtained with the assistance of surfactants [118,119]. Although nano-particles could improve membrane properties, too much of the additives may adversely affect other membrane properties. For example, too high nano-particle content can increase the surface roughness of the nano-composite membrane, leaving the nano-composite membrane prone to biofilm formation [39,106].

5. Conclusion

After reviewing the various problems associated with the use of membrane separators in MFC, the most dominant problems are identified as internal resistance and biofouling. High membrane internal resistance and formation of biofilm layer on the membrane surface seriously degrades the performance of MFCs. The suitability or otherwise of various types of membranes as separators in MFC have also been described in this review. The Nafion® membrane has been identified as the best membrane separator for MFCs. Although membraneless MFCs look promising because of very low resistance, its high oxygen and substrate crossover has led researchers away to continue using membrane separators in MFCs. Recently, nano-composite membranes have attracted much interest in fuel cell application, including MFCs, because MFCs with nano-composite membranes are cheaper and can produce more power than MFCs using Nafion® membranes. In the future, more innovative nano-composite membranes with better properties should be synthesized to replace the currently used membranes. The nano-composite membranes must be cheaper, more hydrophilic, more conductive and non-porous or dense in order to achieve high MFC performance.

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